11.4 Arenes

1 Structure of Benzene

1.1 Kekulé structure and the real structure



Kekulé structures (do not exist) ≠ **real structure**

Shape

C_6H_6: _____ regular hexagon, all bond angles 120°

Bond lengths

All C–C bonds are _____ in length (0.139 nm), between C–C and C=C

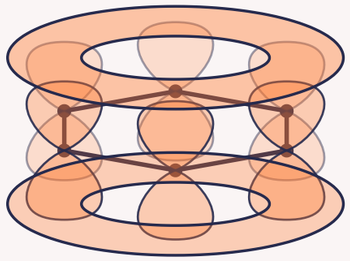
Drawing it

The Kekulé structure (cyclohexatriene) does not exist, the real molecule is drawn with a **circle**

1.2 Delocalisation in benzene

1. Each C is _____ hybridised: it forms three σ bonds (two C–C and one C–H)
2. The unhybridised _____ on each C, containing one electron, is _____ to the plane of the ring
3. Each p orbital overlaps _____ with both neighbours → a continuous ring of 6 delocalised π electrons _____ the ring

π cloud above the ring



and below

1.3 Why is benzene less reactive than an alkene towards electrophiles?

1. In benzene, the π electrons are _____ over six C atoms, so the electron density is _____ than in the localised π bond of C=C
2. → electrophiles are less strongly attracted, reaction also needs the loss of delocalisation in the intermediate → higher E_a, so a catalyst or stronger electrophile is needed

2 Evidence for Delocalisation

2.1 Enthalpy change of hydrogenation

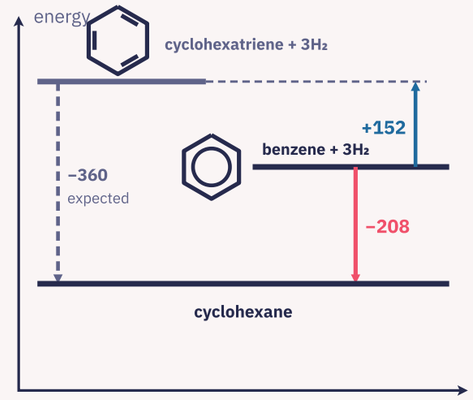
Expected vs actual

Expected for 3 C=C: 3 × (−120) = −360 kJ mol⁻¹

Actual: _____ kJ mol⁻¹

Delocalisation energy

Benzene is _____ kJ mol⁻¹ more stable than cyclohexatriene.



2.2 Bond lengths

Bond	Length / nm
C–C in cyclohexane	0.154
C–C in benzene	_____
C=C in cyclohexene	0.133

The C–C bond length in benzene lies **between** a single and a double bond: each bond has partial double bond character, as the π electrons are delocalised over all six bonds.

2.3 Substitution, not addition

Reagent	Cyclohexene	Benzene
Br_2 in CCl_4, dark	addition	no reaction
HBr(g)	addition	no reaction

Addition would destroy the delocalised π system and its extra stability, substitution _____ it.

3 Naming Arenes



nitrobenzene · methylbenzene · phenol · benzoic acid · benzaldehyde · 2-nitro-methylbenzene

- C_6H_5– is **phenyl**, $C_6H_5CH_2$– is **benzyl**. An alkyl group with more than 6 C: name as phenylalkane (2-phenylheptane).
- **Traditional name**: some groups give the compound a special name, e.g. phenol (–OH), benzoic acid (–CO_2H), benzaldehyde (–CHO), methylbenzene (–CH_3). That group is at **C1**, number the other substituents from it and list them alphabetically.

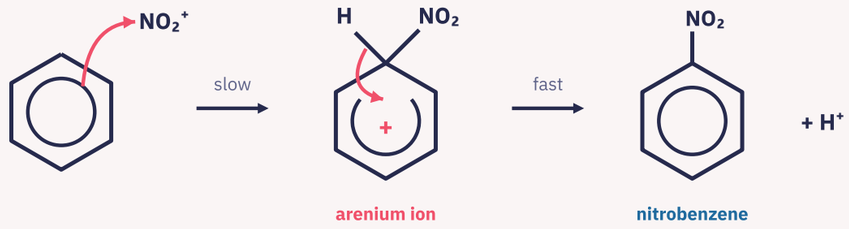
4 Electrophilic Substitution

The delocalised π cloud is a region of _____ → attacked by electrophiles, substitution keeps the ring's stability.

4.1 Mechanism: electrophilic substitution (nitration of benzene)

Reagents and conditions: conc. HNO_3, conc. H_2SO_4, 50 °C

$$HNO_3 + 2H_2SO_4 \rightarrow _____ + 2HSO_4^- + H_3O^+$$



$$H^+ + HSO_4^- \rightarrow H_2SO_4$$

ANSWER STRUCTURE **Describe the mechanism** Name it (electrophilic substitution), write the equation that forms the electrophile, draw every step perfectly with reagents and conditions, curly arrows, the arenium ion and charges, then write the equation that regenerates the catalyst. Write the equations only: no headings such as "forming the electrophile" and no written explanation.

Reaction	Reagents and conditions	Electrophile formed
Nitration	_____, 50 °C (methylbenzene 30 °C, deactivated 70 °C)	NO_2^+
Halogenation	X_2, _____ (or Fe), r.t., dark	$X_2 + FeX_3 \rightarrow X^+ + FeX_4^-$
Friedel–Crafts alkylation	RCl, _____ or $FeCl_3$, r.t.	$RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$
Friedel–Crafts acylation	RCOCl, _____, heat under reflux	$RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$

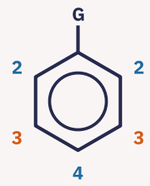


nitrobenzene | chlorobenzene | methylbenzene (R = CH_3) | phenylethanone (RCO = CH_3CO)

FeX_3 and AlX_3 are Lewis acids, regenerated at the end: $H^+ + FeX_4^- \rightarrow HX + FeX_3$. Anhydrous, as they react with water.

5 Effect of Substituents

5.1 Effect on reactivity



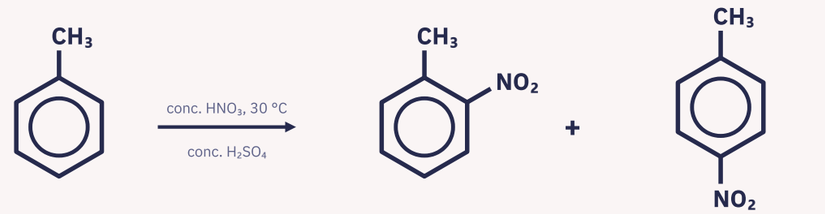
Ring-activating group, e.g. $-CH_3$

1. $-CH_3$ is _____: increases the electron density of the ring → ring more attractive to electrophiles
2. and _____ the carbocation intermediate → faster than benzene

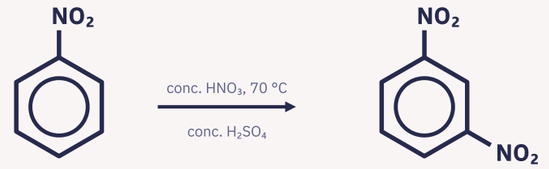
Ring-deactivating group, e.g. $-NO_2$

1. $-NO_2$ is _____: decreases the electron density of the ring → ring less attractive to electrophiles
2. and _____ the carbocation intermediate → slower than benzene

5.2 Directing effect: where the second group goes



methylbenzene → 2-nitromethylbenzene + 4-nitromethylbenzene



nitrobenzene → 1,3-dinitrobenzene

Activating, 2,4-directing
$-CH_3$, $-OH$, $-NH_2$, $-OR$. Electron-donating, e.g. phenol + dil. HNO_3 → 2- and 4-nitrophenol

Deactivating, 3-directing
$-NO_2$, $-CN$, $-CO_2H$, $-CHO$, $-COR$. Electron-withdrawing, slower than benzene

Deactivating, 2,4-directing
Halogens: withdraw by induction, but the lone pair stabilises the 2,4-intermediates

6 Methylbenzene: Ring vs Side Chain

Reaction of methylbenzene	Reagents and conditions	Product	Notes
Ring: electrophilic substitution	Cl_2, _____, r.t., _____		at the 2- and 4-positions ($-CH_3$ is 2,4-directing)
Side chain: free radical substitution	Cl_2, _____		further substitution gives $-CHCl_2$ and $-CCl_3$
Side-chain oxidation	$KMnO_4$, dil. H_2SO_4, _____ or $KMnO_4$, OH^-, heat, then H^+		benzoic acid (white ppt on cooling), needs a _____

Any alkyl side chain with a benzylic H is oxidised to $-CO_2H$ (ethylbenzene also gives CO_2). tert-Butylbenzene has no benzylic H: no reaction. $K_2Cr_2O_7$ is too weak.